High Efficiency Segmented Thermoelectric Unicouples

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Abstract. Highly efficient, segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit are currently being developed at the Jet Propulsion Laboratory (JPL). These segmented unicouples incorporate a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL. They can be integrated into thermoelectric power generation modules which could be used for a variety of applications making use of waste heat recovery and also potentially in Radioisotope Power Systems (RPSs) that may be needed for several NASA missions planned over the next few years. These missions call for electrical power requirements ranging from 20 to 200 watts and 6 to 15 years mission duration. The resulting RPSs would not only have a high specific power (~8 We/kg) that is about twice that of the state-of-the-art Radioisotope Thermoelectric Generators (RTGs), but also a higher overall efficiency (> 14%), halving the $238PuO_2$ needed for a given electric power requirement. These advanced RPSs would couple the novel, segmented thermoelectric unicouples (STUs) to one or several standard General Purpose Heat Source (GPHS) modules (or bricks), depending on the electric power requirements. The advanced STUs would operate at a hot side temperature of about 1000 K, alleviating some of the concerns associated with the high temperature operation of current GPHS-RTGs (~1300K), and at a cold side temperature of ~400 K. The latest developments in the fabrication and testing of the advanced segmented thermoelectric unicouples are presented and discussed.

INTRODUCTION

A segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit has been proposed and described earlier (Caillat, 1998 and 1999a) (Fleurial, 1997a and 1997b). This segmented unicouple, under development at the Jet Propulsion Laboratory (JPL), includes a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at the Jet Propulsion Laboratory (JPL). To achieve high thermal to electrical efficiency, it is desirable to operate thermoelectric generator devices over large temperature differences and also to maximize the thermoelectric performance of the materials used to build the devices. In a segmented unicouple as depicted in Figure 1, each section has the same current and heat flow as the other segments in the same leg. Thus in order to maintain the desired temperature profile (i.e. keeping the interface temperatures at their desired level) the geometry of the legs must be optimized. Specifically, the relative lengths of each segment in a leg must be adjusted, primarily due to differences in thermal conductivity, to achieve the desired temperature gradient across each material. The ratio of the cross sectional area between the n-type and p-type legs must also be optimized to account for any difference in electrical and thermal conductivity of the two legs. A semi-analytical approach that includes smaller effects such as the Peltier and Thompson contributions and contact resistance in order to optimize and calculate the expected properties of the device has been used to solve the problem (Swanson, 1961). For each segment, the thermoelectric properties are averaged for the temperature range it is used. At each junction (cold, hot, or interface between two segments), the relative lengths of the segments are adjusted to ensure heat energy balance at the interface. Without any contact resistance between segments, the efficiency is not affected by the overall length of the device; only the relative length of each segment needs to be optimized. The total resistance and power output, however, does depend on the overall length and cross sectional area of the device. The calculated optimized thermoelectric efficiency is about 15.5% with the hot junction at 975K and the cold junction near room temperature. The optimal geometry is illustrated in Figure 1.

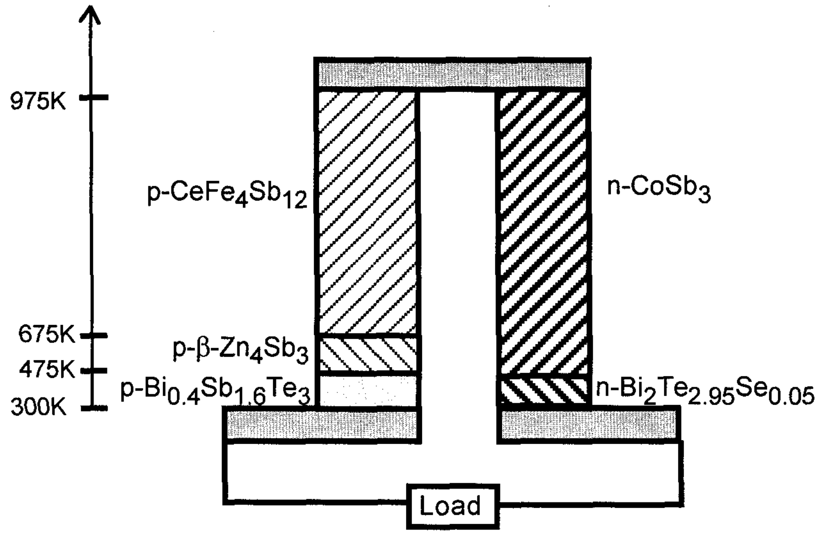

FIGURE 1. Illustration of the advanced unicouple incorporating new high performance thermoelectric materials. The relative lengths of each segment and the cross-sectional areas for the p- and n-legs are drawn to scale. The calculated thermoelectric efficiency is 15.5%.

High contact resistance between the thermoelectric segments can dramatically reduce the efficiency of a generator. Calculations show that a low contact resistance, less than about 20 $\mu\Omega cm^2$, is required to keep the efficiency from being significantly degraded by the contact resistance. Techniques and materials have been developed to bond the different segments of the unicouple together and also the lower and upper segments to the interconnects (Caillat, 1999b). Electrical contact resistance lower than 5 $\mu\Omega cm^2$ have been obtained for each of the junctions at its projected operating temperature.

The hot-side temperature may vary depending on the specific application and this requires a different optimization of the geometry of the legs. However, the bonding techniques and materials developed for the version of the unicouple operating at a hot-side temperature of 975K could be applied for the fabrication of unicouples operating at lower hot-side temperatures. The maximum hot-side operating temperature of the segmented unicouple is presently limited to 975K because of the limited temperature stability of the thermoelectric materials used for the upper segments above about 1075K. Efforts are underway to develop skutterudite based materials which could operate at significantly higher temperatures. Preliminary results obtained on arsenide and phosphide skutterudites show that these materials are more refractory than their antimonide analogs and could therefore potentially be used at higher temperatures. Efforts are underway to fully assess the potential of some of these materials for thermoelectric applications. Figure 2 shows the variations of the calculated thermoelectric efficiency as a function of the hot-side and cold-side temperature for the segmented unicouple shown in Figure 1.

SEGMENTED UNICOUPLE FABRICATION AND TESTING

Both entire n- and p-segmented legs were fabricated by uniaxial hot-pressing of the various thermoelectric materials in powder form separated by thin metallic foils. The n- and p-legs have also been successfully connected to a "cold shoe" for heat transfer to the heat sink using a Bi-Sn solder and Ni as a diffusion barrier. Each leg was soldered to a Cu block which was itself soldered to a Cu plated Al_2O_3 plate etched in the center to avoid an electrical short between the two thermoelectric legs (see Figure 3). A Nb heater was fabricated to match the top diameter of the p- and n-legs put together. It was made out of a Nb housing containing a Ta heating element cemented in a refractory and electrically insulating cement. This Nb heater, shown in Figure 3, was designed to be used as the top interconnect during the test. The Nb heater was brazed to the top of the segmented legs during the test by raising the

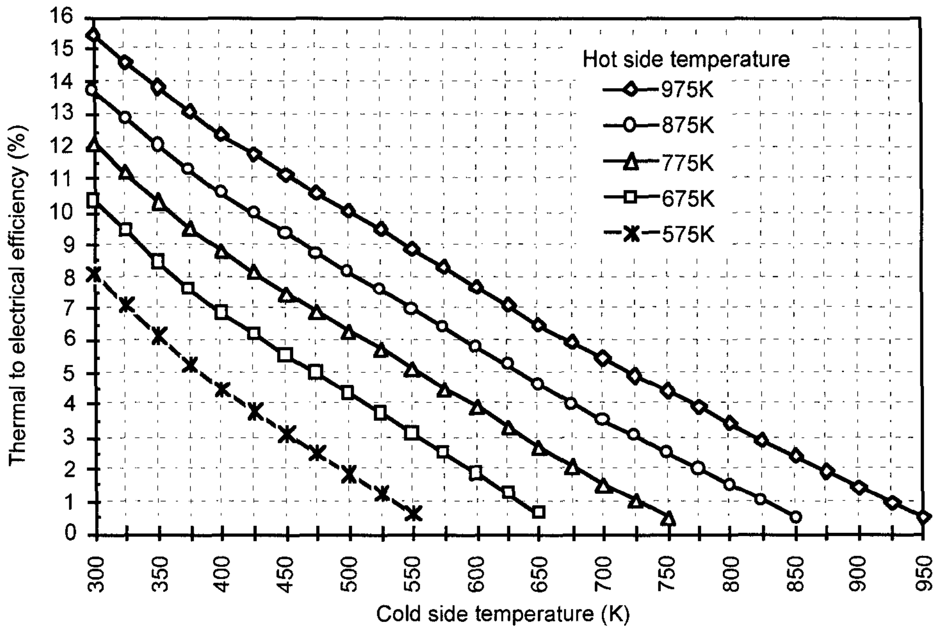

FIGURE 2. Calculated Thermal to Electrical Efficiency as a Function of Cold-Side and Hot-Side Temperature for the Segmented unicouple as Shown in Figure 1.

temperature of the heater up to about 973K. The unicouple was mounted onto a water cooled Cu base plate to achieve the desired thermal gradient during the test (see Figure 4). It was also instrumented with several thermocouples to measure the hot-side and cold-side temperature during the test. The entire assembly was set-up in a vacuum chamber and the thermal and electrical testing was conducted in 10^{-5} Torr vacuum to minimize heat losses by conduction. In order to minimize heat losses by radiation , a multi-foil, circular Mo heat shield was fabricated and was installed around the upper portion of the n- and p-legs (not shown in Figure 4). The hot-side temperature

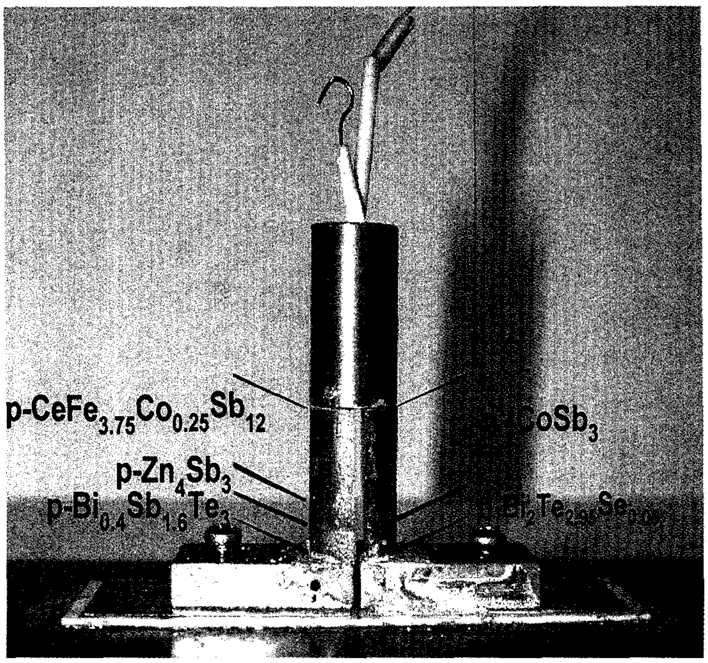

FIGURE 3. Segmented Unicouple Fabricated for Electrical and Thermal Testing. See Text for Fabrication Details.

(measured inside the top of the legs) was progressively increased to 923K while the cold-side temperature was maintained at 300K. The I-V curve of the segmented unicouple is shown in Figure 5. The measured open circuit voltage is about 210 mV and a maximum power output of about 520 mW was obtained at half the open circuit voltage. An internal resistance of 20 mΩ was calculated for the unicouple. The calculated power output and internal resistance were 1.4 W and 9.8 mΩ, respectively. Post-testing examinations of the unicouple revealed that the larger value of the internal resistance compared to the predicted value was due to an electrical contact resistance between the Nb heater and the top skutterudite segments. The power output was therefore smaller than the predicted. The unicouple was tested for about 48 hours with a steady power output. Future efforts will focus on improving the brazing process at the hot-side interface to achieve an internal resistance close to optimal. In addition, several configurations are being developed in order to estimate the efficiency of the unicouple. In one of these, a sample material of known thermal conductivity would be introduced between the heater and the top thermoelectric materials segments and thermocouples would be introduced inside the top and bottom of this reference sample to measure the heat flux going into the unicouple.

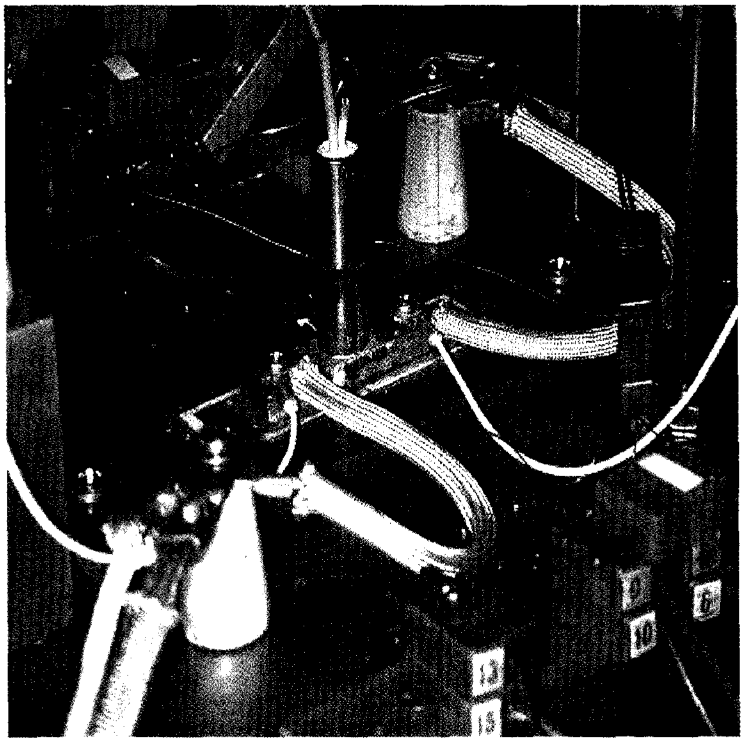

FIGURE 4. Segmented Unicouple Pictured in the Thermal and Electrical Testing Station.

POTENTIAL APPLICATIONS

The advanced segmented unicouples currently being developed could be integrated in a variety of applications including those making use of waste heat. There is a growing interest for waste heat recovery power generation, using various heat sources such as the combustion of solid waste, geothermal energy, power plants, and other industrial heat-generating processes. Hot-side temperatures ranging from 370 to 1000K have been cited in the literature. Because of the need for cleaner, more efficient cars, car manufacturers worldwide have also expressed interest for using waste heat generated by the vehicle exhaust to replace or supplement the alternator. If successful, more power would become available to the wheels and the fuel consumption would decrease. According to some car manufacturers, the available hot-side temperature range would be from 675 to 975K.

Advanced Radioisotope Power Systems (ARPSs) may be needed for several NASA missions planned over the next few years. These missions call for electrical power requirements ranging from 20 to 200 watts range and 6 to 15 years mission duration. The advanced segmented unicouples could be integrated into advanced RTGs, replacing the

Si-Ge unicouples used until now. Preliminary estimates show that the resulting RTGs operating at a hot-side temperature of about 975K and rejection temperature of about 400K would have a high specific power (~8 We/kg) that is about twice that of the state-of-the-art RTGs and a high overall efficiency (> 12%), halving the $238PuO_2$ needed for a given electric power requirement. For example, only 4 GPHS bricks would be needed to provide 100We compared to 7 in a traditional RTG. With the exception of the radiator fins, minimal modifications of the Si-Ge RTGs design can be expected for integrating the advanced segmented unicouples into a more efficient system. Proving that advanced thermoelectric materials can be developed to operate at temperatures up to 1173K, specific power as high as 10 We/kg could be achieved.

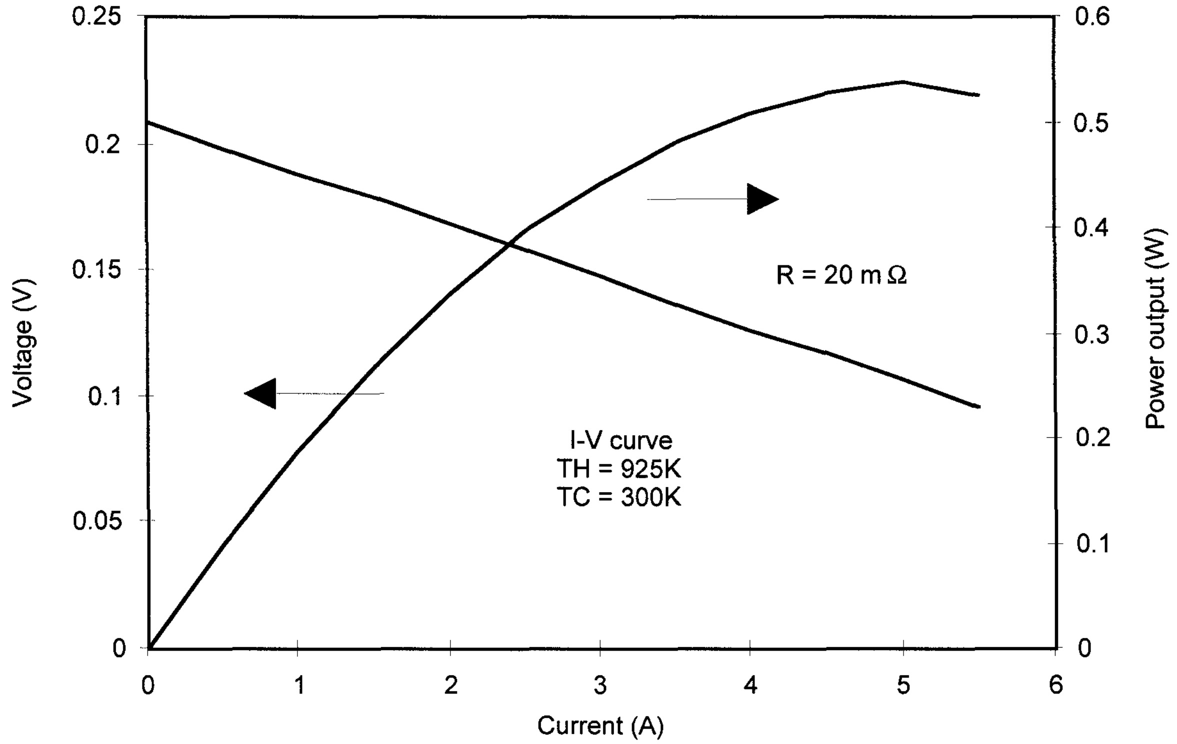

FIGURE 5. I-V Curve for the Advanced Segmented Unicouple.

CONCLUSION

A new version of a segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit is currently under development at JPL. The advanced segmented unicouple would operate over a 300 to 975K temperature difference and the predicted efficiency is about 15.5%. Techniques and materials have been developed to achieve low electric resistance bonds between the different segments of the unicouple and also between the lower and upper segments to the interconnects. Initial thermal and electrical tests have been reported in this paper. Various fabrication and testing materials and techniques are under development in order to estimate the efficiency of the advanced unicouples and demonstrate their superior performance. These segmented unicouples could be applied in a variety of applications making use of waste heat recovery and also possibly in advanced radioisotope power systems.

ACKNOWLEDGMENTS

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